Competitive adsorption of Pb(II), Cu(II) and Zn(II) onto xanthate-modified magnetic chitosan

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ABSTRACT

The competitive adsorption of Pb(II), Cu(II) and Zn(II) onto a novel xanthate-modified magnetic chitosan (XMCS) was systematically investigated in single and ternary metal systems. In single system, equilibrium studies showed that the adsorption of Pb(II), Cu(II) and Zn(II) followed the Langmuir model and the maximum adsorption capacities were found to be 76.9, 34.5 and 20.8 mg/g, respectively. In ternary system, the combined action of the metals was found to be antagonistic and the metal sorption followed the order of Pb(II) > Cu(II) > Zn(II); the Langmuir isotherm fitted the data of Pb(II) and Cu(II) well while the isotherm data of Zn(II) correlated well with the Freundlich model. The Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectra (XPS) studies showed that the thiol and amino group participated in the adsorption of Pb(II), Cu(II) and Zn(II).

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1. Introduction

Toxic heavy metal pollution is one of the most significant environment problems. The metals are of special concern because they are non-degradable and therefore persistent. Numerous techniques have been developed for the clean-up of waters contaminated with heavy metals. In comparison with such conventional technologies as chemical precipitation, ion exchange, membrane filtration, electrolytic methods, and solvent extraction, adsorption is regarded as one of the most effective and attractive process with several advantages associated with no chemical sludge and high removal efficiency [1,2].

Magnetic chitosan has been regarded as a promising adsorbent. It has several advantages. This material has strong metal chelating capability due to the presence of the amine and hydroxyl groups in chitosan chain. Also, it can easily be separated from sorption system by using magnetic field due to magnetic properties. Although lots of research works have been focused on the application of magnetic chitosan for the metal removal from the aqueous media [3–6], to our knowledge, only a few of manuscripts are dedicated to the competitive adsorption from the binary or multiple aqueous solutions.

As a matter of fact, it is more important to evaluate the simultaneous adsorption behavior and interactions involving two or more metal species since sole toxic metal species rarely exist in natural streams and waste effluents [7–9].

Furthermore, to improve the adsorption capacity, we modified magnetic chitosan using xanthate. The introduction of thiol group on xanthate-modified magnetic chitosan (XMCS) may enhance the interaction with heavy metals in solution and increase the adsorption ability.

In this study, a novel xanthate-modified magnetic chitosan (XMCS) has been developed for the removal of Pb(II), Cu(II), Zn(II) in single and ternary solutions. The main objective of the study was to determine the adsorption capacity of XMCS in single and ternary system, to establish the applicable isotherm model and to elucidate the sorption mechanism.

2. Materials and methods

2.1. Chemicals and materials

Chitosan flakes (85% deacetylated) used in the experiments were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. $Pb(NO_3)_2$, $Cu(NO_3)_2·3H_2O$, $Zn(NO_3)_2·6H_2O$ were of analytical grade and used as sources for metal ions. Stock solution (1000 mg/L) of each metal ion was prepared in distilled water. CS_2 was also of analytical grade and the non-volatile matter was less than 0.002%.

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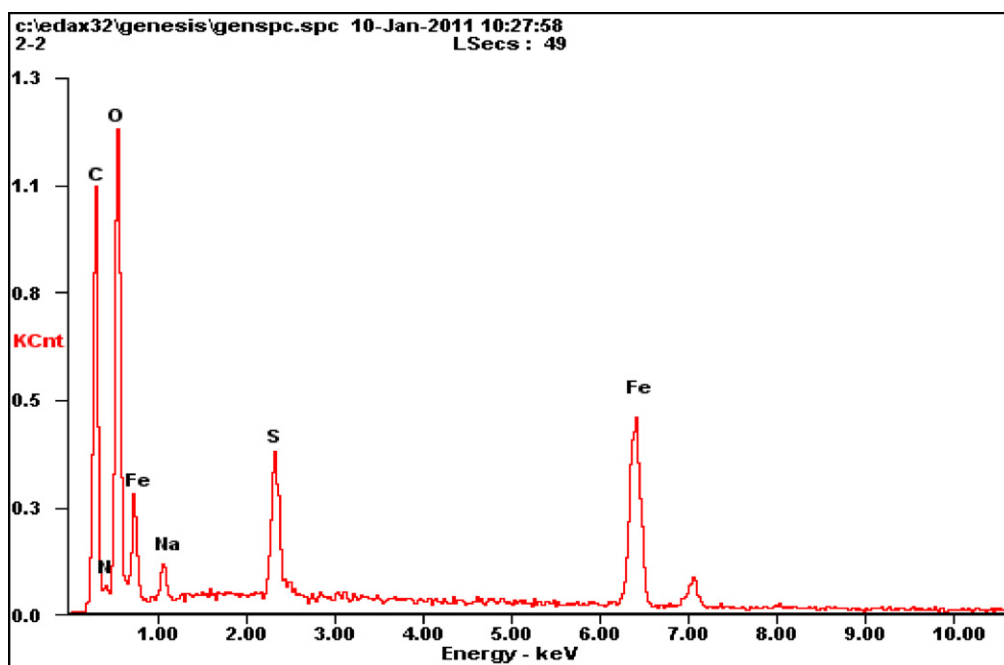
Fig. 1. The EDS spectra of XMCS.

2.2. Preparation of magnetic chitosan (MCS)

Chitosan flakes were added into 100 mL 3% (v/v) acetic acid in a beaker to obtain chitosan solution and the mixture placed overnight. $FeSO_4$ and $FeCl_3$ were dissolved in 1:2 molar ratio and the resulting solution was dropped into 30% (w/v) sodium hydroxide, mechanically stirred for 3 h. The beads were collected and washed with distilled water until reaching neutrality. Then the magnetic chitosan beads were cross-linked with glutaraldehyde [10]. The wet beads were suspended in 0.05 M glutaraldehyde solution to obtain a ratio of 1:1 with chitosan. The chitosan beads in resulting glutaraldehyde solution were left standing for 24 h at room temperature. After 24 h the cross-linked magnetic chitosan beads were intensively washed with distilled water, filtered and dried in vacuum at 70 °C. The newly formed beads were ground to a constant particle size (<84 μm) before use. The following reaction showed the preparation of magnetic particles:

$$Fe^{2+} + 2Fe^{3+} + 8H_2O \rightarrow Fe_3O_4 + 4H_2O$$
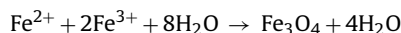
2.3. Modification of magnetic chitosan with xanthate (XMCS)

Grafting of thiol groups was carried out according to the procedure described by Kannamba et al. [11] with chitosan flakes. The cross-linked magnetic chitosan (2 g) were treated with 100 mL of 14% NaOH solution and 1 mL of CS_2. The mixture was stirred at room temperature for 24 h. The product was washed thoroughly with distilled water, dried in vacuum at 70 °C and ground to a constant particle size (<84 μm) before used in the experiments.

2.4. Characterization of XMCS

Chemical composition of samples was determined by energy dispersive X-ray spectrometer (EDS). Fourier transform infrared spectroscopy (FTIR) spectra of XMCS before and after adsorption of Pb(II), Cu(II), Zn(II) were recorded using FTIR spectrometer (Spectrum GX, Perkin-Elmer) connected with a computer. Samples were prepared in KBr disks. X-ray photoelectron spectra (XPS) of XMCS

before and after Pb(II), Cu(II), Zn(II) adsorption were obtained by using PHI Quantera SXM XPS spectrometer. Computer deconvolution was applied to detect the elemental peaks present in the XMCS.

2.5. Adsorption isotherms

Adsorption equilibrium isotherms for single and ternary systems of Pb(II), Cu(II) and Zn(II) ions were all performed at the optimum pH-value of 5.0 and temperature at 25 °C 150 rpm.

For single system, certain dosage of 20 mg sorbent was mixed with 15 mL of aqueous solutions of Pb(II), Cu(II) and Zn(II) (only Pb(II) or Cu(II) or Zn(II) ions present) with certain initial concentrations (C_0, mg/L) ranging from 25 mg/L to 250 mg/L.

For ternary system, the same dosage of 20 mg sorbent was mixed with 15 mL of composite solutions containing equimolar concentrations of each metal ions (Pb(II), Cu(II) and Zn(II)) in the range of 25–250 mg/L.

Each of the three metal concentrations was determined by atomic absorption spectrometric method with flame atomization (AAS 6 Vario). All experiments were conducted three times.

The adsorbed amount of metal ion per unit weight at time t, q_t (mg/L) was calculated from the mass balance equation as

$$q_t = \frac{(C_0 - C_t)V}{m}$$

where C_0 and C_t (mg/L) are the initial metal ion concentration and the metal ion concentration at any time t, respectively; V is the volume of the metal ion solution; and m is the weight of XMCS.

3. Results and discussion

3.1. Characterization of XMCS

Amine groups of chitosan are the potential functional groups, which complex with toxic metal ions during the adsorption process. In present study, a new thiol group was introduced and cross-linked with glutaraldehyde in order to improve the adsorption capacity
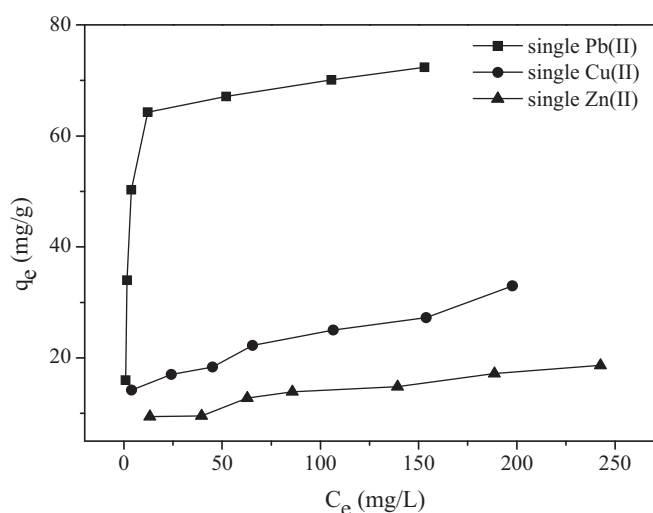
Fig. 2. Equilibrium adsorption isotherms of Pb(II), Cu(II) and Zn(II) by XMCS in single system.

and resistance to solubility in acid media. XMCS was characterized by EDS spectra analysis.

EDS spectra were used to identify the existence of a particular element in a material [12,13]. The EDS spectrum of XMCS is presented in Fig. 1, which showed the peaks of C, O, N, Fe, they were four major constituents of chitosan and magnetite. Also, there was a peak corresponding to S element, confirming that the magnetic chitosan (MCS) was modified by xanthate successfully.

3.2. Adsorption isotherms of single metal solutions

Based on our previous studies [14], the chemical modification of magnetic chitosan with xanthate did improve the adsorption capacity of heavy metals. XMCS showed higher adsorption capacities of Pb(II), Cu(II), Zn(II) compared to unmodified magnetic chitosan (MCS) (data not shown). In this paper, we focused on the adsorption properties of Pb(II), Cu(II) and Zn(II) by XMCS, not the comparison of adsorption capacity by MCS and XMCS.

Fig. 2 gives the adsorption equilibrium isotherms obtained for Pb(II), Cu(II) and Zn(II) ions by XMCS. A relationship was observed between the amount of metal ion adsorbed on the adsorbent and the remaining metal ion concentration in aqueous phase at equilibrium. It was shown that the adsorption capacity increased with the equilibrium concentration of the metal ion in solution, progressively saturating the adsorbent.

For interpretation of the adsorption data, the Langmuir and the Freundlich isotherm models were used. The linear form of the Langmuir isotherm is given by

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m}$$

where q_e and C_e are the amount adsorbed (mg/g) and the adsorbate concentration on solution (mg/L), both at equilibrium; k_L (L/mg) is the Langmuir constant related to the energy of adsorption; and q_m (mg/g) is the maximum adsorption capacity for monolayer formation on adsorbent.

The linearized Freundlich form is

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e$$

where k_F and n are constants for the Freundlich isotherm, they are indicative of the adsorption capacity (mg/g) and adsorption intensity.

Table 1
Adsorption isotherm model constants for single metal system.

	The Langmuir isotherm constants		
	k_L (L/mg)	q_m (mg/g)	R^2
Pb(II)	0.394	76.9	0.999
Cu(II)	0.0372	34.5	0.957
Zn(II)	0.0274	20.8	0.977
	The Freundlich isotherm constants		
	k_F (mg/g)	n	R^2
Pb(II)	27.0	2.93	0.740
Cu(II)	4.90	9.69	0.883
Zn(II)	4.47	1.64	0.903

The calculated Langmuir and Freundlich constants are shown in Table 1. For the three studied systems, the Langmuir isotherm correlated better than Freundlich with the experimental data (Fig. 3), suggesting a monolayer adsorption. The maximum adsorption values were 76.9, 34.5 and 20.8 mg/g for Pb(II), Cu(II) and Zn(II) ions, respectively. The Langmuir isotherm constants, q_m and k_L, followed the order of Pb(II) > Cu(II) > Zn(II). Pb(II) having the highest k_L value suggested the highest affinity to bind to the functional groups, resulting to maximum monolayer adsorption capacity over Cu(II) and Zn(II).

For the adsorption of Pb(II), Cu(II) and Zn(II), Chen et al. [15] reported that the maximum adsorption capacities (q_m) were 35.5, 34.1, 10.2 mg/g for Cu(II), Pb(II) and Zn(II) respectively, using the cross-linked chitosan with epichlorohydrin. And the selectivity order of Cu(II), Pb(II) and Zn(II) was Cu(II) > Pb(II) > Zn(II), which was not agreement with the order observed in this study.

3.3. Adsorption isotherms of ternary metal solutions

The adsorption equilibrium isotherms obtained for Pb(II), Cu(II) and Zn(II) ions by XMCS in ternary system are shown in Fig. 4. It can be seen that the adsorption capacity followed the order as Pb(II) > Cu(II) > Zn(II), which was consistent with the order in single systems.

For ternary system, the original Langmuir and Freundlich isotherm equations were applied to determine the effect of presence of other metal ions on the isotherm constants. Other studies
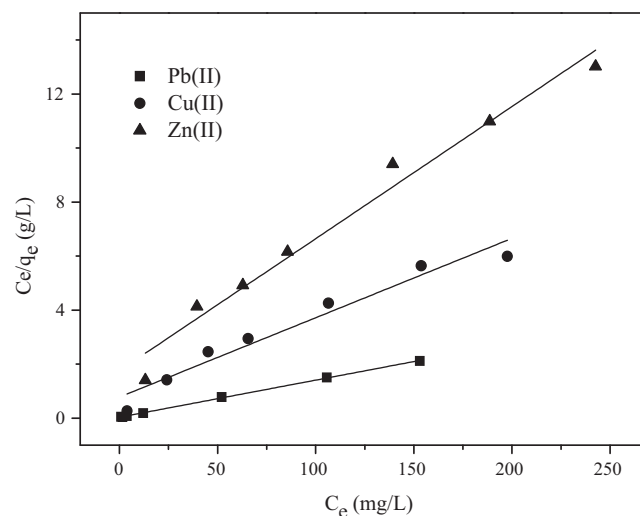

Fig. 3. Langmuir isotherm model fitted for the adsorption of Pb(II), Cu(II) and Zn(II) by XMCS in single system.
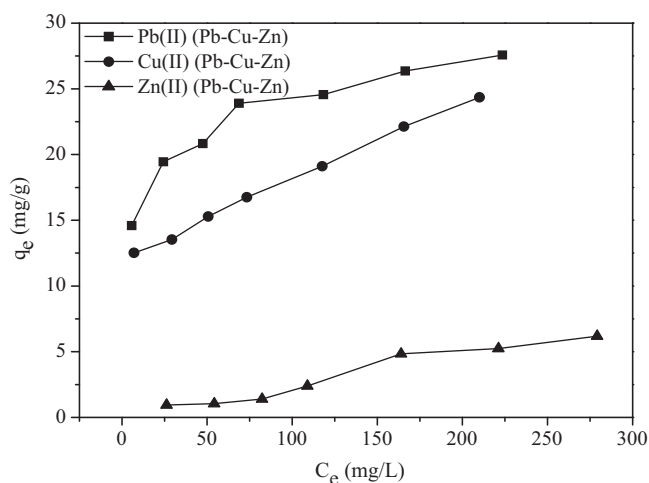
Fig. 4. Equilibrium adsorption isotherms of Pb(II), Cu(II) and Zn(II) by XMCS in ternary system.

also used the original Langmuir and Freundlich models to fit the experimental data in binary and ternary systems [16,17].

The isotherm constants for Pb–Cu–Zn system are listed in Table 2. For Pb(II) and Cu(II), the Langmuir isotherm fit the data well with high correlation coefficients. For Zn(II), the isotherm data correlated well with the Freundlich model, even the correlation coefficient of the Freundlich model was only 0.909. Fig. 5 illustrates that the experimental data of Pb(II) and Cu(II) in ternary system were in good agreement with the Langmuir model while Zn(II) was an acceptable fit with the plot of the Freundlich model.

The mutual interference effects of metal ions on adsorption were probed using q'_e/q_e ratios, the q_e and q_e, indicate the adsorption capacity at equilibrium in single and ternary systems. The value of q'_e/q_e will imply whether the effect of mixing metals in a solution is synergistic ($q'_e/q_e > 1$), no net interaction ($q'_e/q_e = 1$), or antagonistic ($q'_e/q_e < 1$) [18]. The q'_e/q_e values of Pb(II), Cu(II) and Zn(II) in ternary system were 0.381, 0.739, 0.333, respectively. All the values were less than 1, implying that the adsorption of metal ions was suppressed by the presence of other metals in the solution. An antagonistic effect was exerted by the metal ions on others adsorption capacity.

Futalan et al. [16] reported the comparative and competitive adsorption of copper, lead and nickel using chitosan immobilized on bentonite. The adsorption data of single and binary systems indicated that Cu(II) and Pb(II) best fit the Freundlich isotherm while Ni(II) followed the Langmuir model. In binary system, the adsorption capacities was in the same order of Pb(II) > Cu(II) > Ni(II) as in single systems. Prasad et al. [19] studied the multi-component sorption of Pb(II), Cu(II) and Zn(II) onto low-cost mineral adsorbent

Table 2
Adsorption isotherm model constants for ternary metal system.

	The Langmuir isotherm constants		
	k_L (L/mg)	q_m (mg/g)	R^2
Pb(II)	0.0355	28.6	0.996
Cu(II)	0.0823	26.3	0.97
Zn(II)	–	–	1E−05

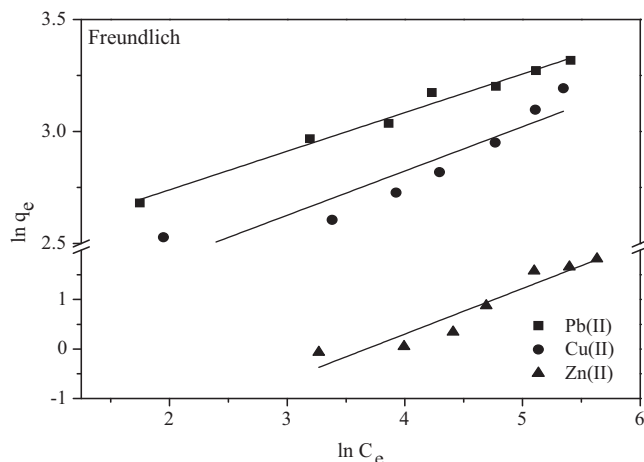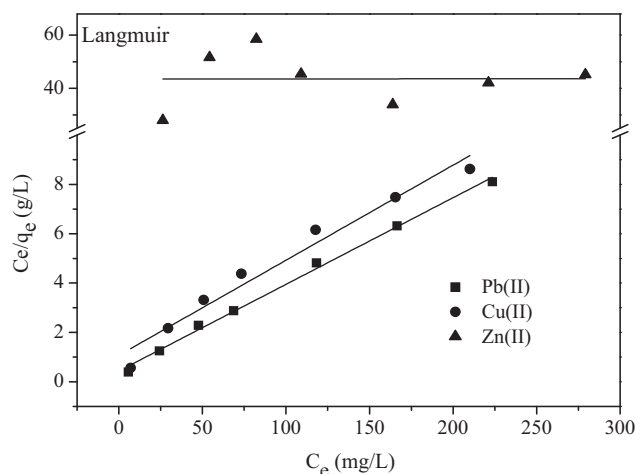|	The Freundlich isotherm constants		
	k_F (mg/g)	n	R^2
Pb(II)	11.0	5.81	0.985
Cu(II)	7.63	5.08	0.875
Zn(II)	0.0339	1.09	0.909

Fig. 5. Langmuir and Freundlich isotherm model fitted for the adsorption of Pb(II), Cu(II) and Zn(II) by XMCS in ternary system.

using batch-type sorption experiments. The adsorption capacities of Pb(II), Cu(II) and Zn(II) followed the same order both in single system and ternary system. In ternary system, Cu(II) and Zn(II) were well fit both by the Langmuir and the Freundlich models while Pb(II) correlated better with the Langmuir model. And the comparison of adsorption capacity of low-grade phosphate rock decreased in multi-component system as compared to single component due to ionic interaction. Adsorption properties for Cu(II), Pb(II) and Cd(II) onto an iminodiacetic acid (IDA) chelating resin were investigated at the optimal pH-value in both single and binary solutions using batch experiments by Li et al. [9]. The maximum adsorption capacity in single system for Cu(II), Pb(II) and Cd(II) was calculated to be 2.27, 1.27 and 0.65 mmol/g individually. The modified Langmuir model could described the binary competitive adsorption behavior successfully and the IDA-chelating resin possessed a good selectivity toward Cu(II) over Pb(II) and Cd(II). Liu et al. [20] studied the competitive adsorption of heavy metals on peat. The results showed that the adsorption isotherm fit the Langmuir model very well. The adsorption capacities followed the order of Cu(II) > Ni(II) > Cd(II) in single-component systems and the competitive adsorption capacities fell in the decreasing order Cu(II) > Ni(II) > Cd(II) in multi-component systems.

However, several studies showed that the adsorption capacity order was not consistent in single and multi-component sorption. Liu et al. [21] reported the selective removal of copper and lead ions by diethylenetriamine-functionalized adsorbent (P-DETA). In the single metal species system (only copper or lead ions present),
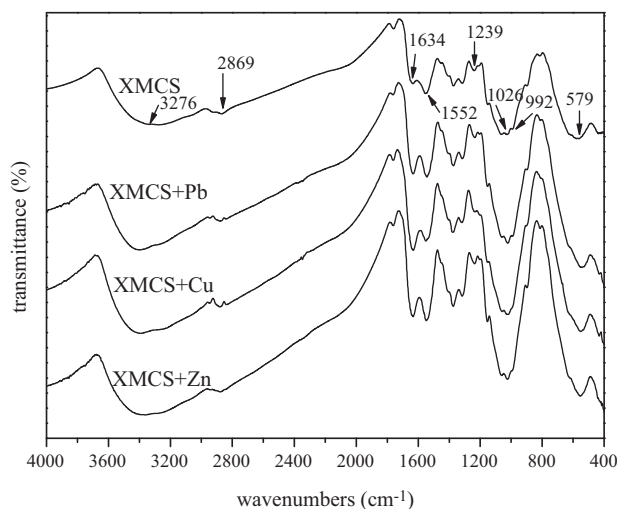
Fig. 6. FTIR spectra of XMCS before and after adsorption of Pb(II), Cu(II), Zn (II).

P-DETA was found to adsorb copper ions or lead ions significantly (with a slightly higher adsorption uptake capacity for lead ions than copper ions). However, P-DETA displayed an excellent selectivity in the adsorption of copper ions over lead ions in the binary metal species system (with both copper and lead ions present). Mahamadi and Nharingo [18] studied the competitive adsorption of Pb(II), Cd(II) and Zn ions onto *Eichhornia crassipes* in binary and ternary systems. The combined action of the metals was found to be antagonistic, and the metal sorption followed the order of Pb(II) > Cd(II) > Zn(II) in single system. However, the biosorption affinity followed the order of Pb(II) ≫ Zn(II) > Cd(II) in ternary system.

3.4. Adsorption mechanism of Pb(II), Cu(II) and Zn(II) on XMCS

To elucidate the mechanism, the surface interactions involved in the adsorption process (with pH 5.0) were examined. FTIR spectra have been a useful tool in identifying the existence of certain functional groups in a molecule as each specific chemical bond often shows a unique energy absorption band. Fig. 6 shows the FTIR spectra of XMCS before and after adsorption of Pb(II), Cu(II) and Zn(II). For the spectrum of XMCS, The peak at 579 cm^{-1} corresponds to Fe—O group, proving the existence of the Fe$_3$O$_4$. The peaks at 3276 cm^{-1} and 2869 cm^{-1} are attributed to O—H stretching vibration and C—H stretching vibration, respectively. The absorption bands at 1153 cm^{-1} (asymmetric stretching of the C—O—C bridge), 1239 cm^{-1} (C—N stretching), 1026 cm^{-1} (skeletal vibrations involving C—O stretching) are characteristics of chitosan's saccharide structure [22,23]. The band at peak of 1552 cm^{-1} for XMCS can be assigned to the —NH group in amine. The XMCS exhibited peak attributed to νC=S at 992 cm^{-1}. The peak for C—S—S and C—O—C symmetric stretching seems to have merged into a broad band at 1026 cm^{-1} [24]. After adsorption of Pb(II), Cu(II) and Zn(II), significant changes in the FTIR spectra were found at the wave numbers of 1552 cm^{-1}, 1239 cm^{-1} and 992 cm^{-1}. The reduction of the intensities at 1239 cm^{-1} (C—N stretching) and the changes of 1552 cm^{-1} (assigned to the —NH group in amine) indicated that nitrogen atoms are the adsorption sites for metal adsorption on XMCS. Similar behaviors were reported by Zhou et al. [25] and Li and Bai [26]. The disappearance of peak 992 cm^{-1} which is associated with thiol group was indicative of the role of thiol group in the complexation with Pb(II), Cu(II) and Zn(II) ions. So it can be concluded that the adsorption sites are the nitrogen atoms of the amino group in chitosan and the sulfur atoms of attached xanthate group. This conclusion was consistent with the studies by Chauhan and

Sankararamakrishnan [27]. They concluded that thiol and amino groups participate in the Pb(II) adsorption process.

To further investigate the interactions between Pb(II), Cu(II), Zn(II) and XMCS. XPS studies of XMCS before and after metal adsorption were conducted. The XPS spectra of C1s, O1s and Fe 2p before and after adsorption did not show any noticeable change, indicating that these atoms were not involved in the chemical adsorption of Pb(II), Cu(II) and Zn(II). But the computer deconvolution of XPS spectra of N1s and S2p showed the significant changes, shown in Figs. 7 and 8. For the N 1 s spectra, before adsorption, there was only one peak at 399.5 eV, attributed to the N atom in the —NH$_2$ and C=N groups on the surfaces of the chitosan [28]. After adsorption, however, new peaks at 402.3, 401.6 and 402.7 were observed for Pb(II), Cu(II) and Zn(II), respectively. Similar behavior was reported by Jin and Bai [29]. And the results were also close to the previous reference in which the peaks are at 400.2 eV and 402.1 eV after Cu(II) adsorption by magnetic chitosan [25]. This indicated that some N atoms existed in a more oxidized state due to metal adsorption. This phenomenon can be attributed to the formation of —NH$_2$···M(II) (M = Pb, Cu, Zn) complexes, in which a lone pair of electrons in the nitrogen atom was donated to the shared bond between the N and Pb(II), Cu(II) or Zn(II). So the XPS spectra provided evidence of metal binding to nitrogen atoms.

The computer deconvolution of the XPS spectrum of S2p shows two peaks before adsorption at the binding energy (BE) of 162.7 and 168.1 eV, corresponding to the thiol group and some oxidized sulfur [30]. However, after adsorption, new peaks at 164.2, 164.1 and 164.8 were observed for Pb(II), Cu(II) and Zn(II), respectively. Kannamba et al. [11] also found that the computer deconvolution of the XPS spectrum of S2p showed a binding energy shift from 162.94 eV to 163.44 eV after adsorption of Cu(II) by ECXCs. This indicated that the sulphur of thiol group on XMCS was involved in chemisorption of Pb(II), Cu(II) and Zn(II) ions. The studies on the adsorption of Pb(II) and Cd(II) on thiol-functionalized silica also showed the participation of sulphur of thiol in complexation with heavy metals through XPS spectral analysis[30].

Therefore, both FTIR spectra and XPS spectra provided the evidence that Pb(II), Cu(II) and Zn(II) are mainly through forming coordination bonds with the nitrogen atoms and sulfur atoms in XMCS.

3.5. Selective adsorption mechanisms

Although both FTIR and XPS studies revealed the adsorption mechanism that Pb(II), Cu(II) and Zn(II) formed complexes with the nitrogen atoms and sulfur atoms of XMCS, the mechanism cannot be effectively used to explain the selective adsorption behaviors of Pb(II), Cu(II) and Zn(II) on XMCS. Comparing the characteristic properties of Pb(II), Cu(II) and Zn(II), the differences in covalent index ($X_m^2 r$, where X_m is electronegativity and r is ionic radius) may be the reason causing the selective adsorption of Pb(II), Cu(II) and Zn(II) by XMCS. $X_m^2 r$ was a measure for a metal ion of the importance of covalent interactions relative to ionic interactions. According to the Nieboer and Richardson [31], the larger the $X_m^2 r$, the more characteristics of soft acids (HSAB theory), and the metal ions preferentially interacted with the functional group in the following order: S > N > O containing group. The covalent index decreased in the following order: Pb (6.41) > Cu (2.64) > Zn (2.04), suggesting that Pb(II) has a stronger attraction than Cu(II) and Zn(II) to the lone pair of electrons in sulfur atoms and nitrogen atoms to form complexes [32]. Vijayaraghavan et al. [33] studied the application of *Sargassum* biomass to removal heavy metal ions from synthetic multi-metal (Pb(II), Cu(II), Zn(II) and Mn(II)) solutions, they also confirmed that both electronegativity and ionic radii determine the order of preference of metal binding onto alginate.
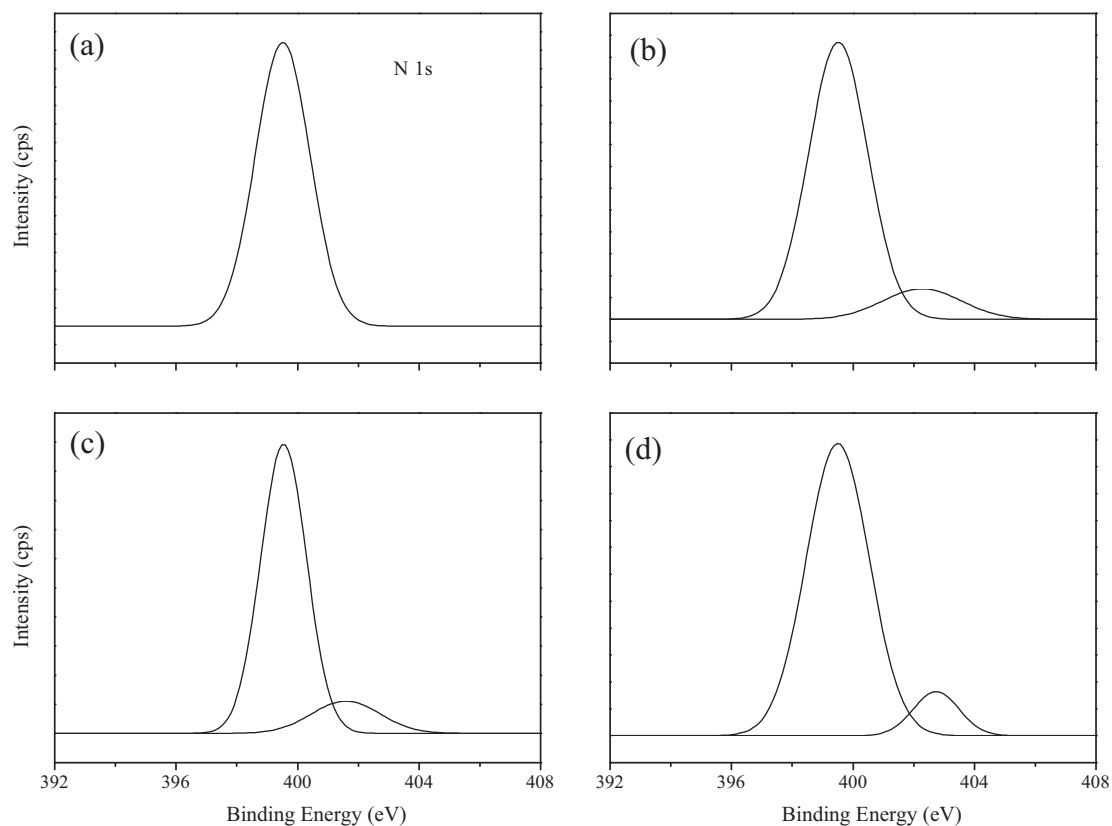
Fig. 7. N1s spectra of XMCS (a) before adsorption; and (b) after adsorption of Pb(II); (c) after adsorption of Cu(II); and (d) after adsorption of Zn (II).
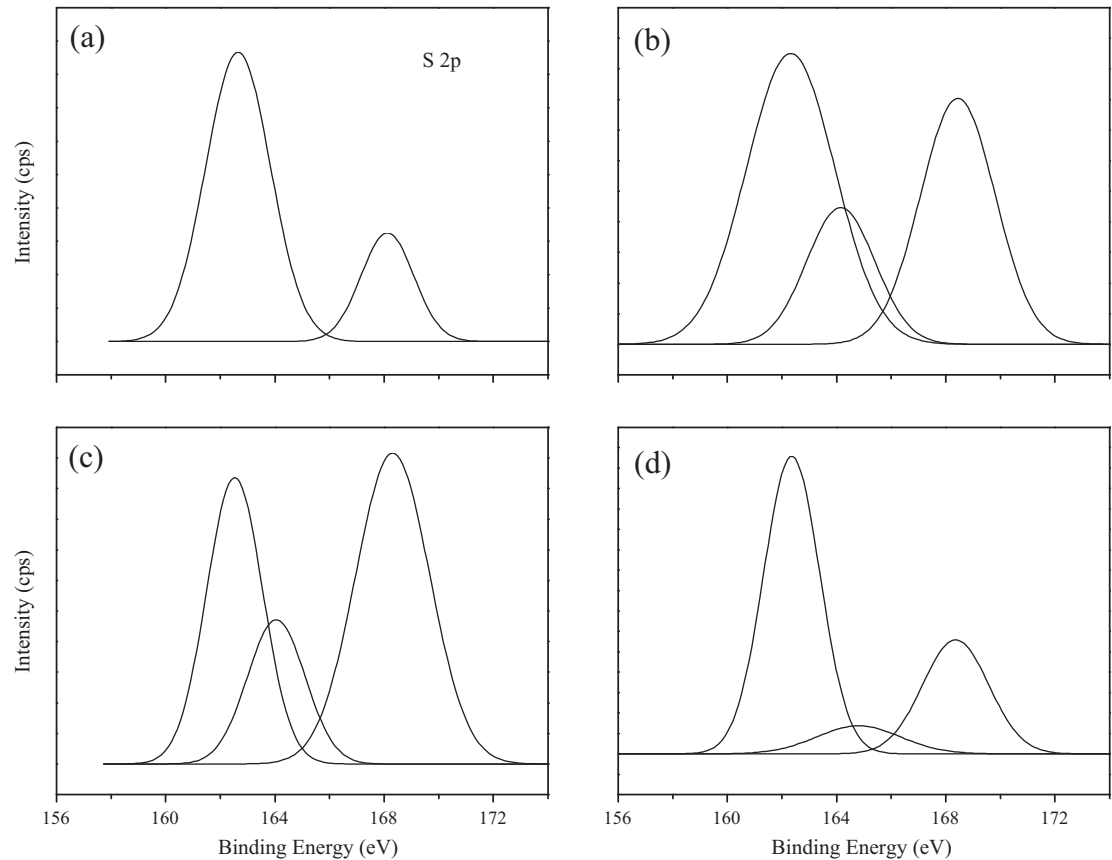
Fig. 8. S2p spectra of XMCS (a) before adsorption; (b) after adsorption of Pb(II); (c) after adsorption of Cu(II); and (d) after adsorption of Zn (II).

4. Conclusions

Adsorption of Pb(II), Cu(II) and Zn(II) was performed for single and ternary systems using a novel xanthate-modified magnetic chitosan (XMCS) as adsorbents. The adsorption capacity was higher for Pb(II) than Cu(II) and Zn(II) for single and ternary systems. The isotherm studies indicated that Pb(II) and Cu(II) followed the Langmuir model both in single and ternary system while Zn(II) followed the Langmuir model in single system and the Freundlich model in ternary system. The FTIR and XPS spectra provided the evidence that Pb(II), Cu(II) and Zn(II) were mainly through forming coordination bonds with the nitrogen atoms and sulfur atoms in XMCS. The differences in covalent index may be the reason causing the selective adsorption of Pb(II), Cu(II) and Zn(II) by XMCS.

Acknowledgment

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